



⑪ Publication number : **0 675 161 A1**

⑫

EUROPEAN PATENT APPLICATION

⑰ Application number : **95302025.2**

⑸ Int. Cl.⁶ : **C08L 7/00, C08L 9/00,
B60C 9/20**

⑱ Date of filing : **27.03.95**

⑳ Priority : **28.03.94 JP 57485/94**

㉑ Date of publication of application :
04.10.95 Bulletin 95/40

㉒ Designated Contracting States :
DE FR GB

㉓ Applicant : **Sumitomo Rubber Industries Ltd.**
6-9, 3-chome, Wakinohama-cho,
Chuo-ku
Kobe-shi, Hyogo 651 (JP)

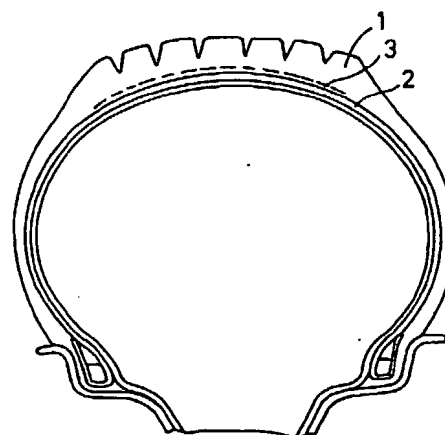
㉔ Inventor : **Nakada, Yoko**
5-1-516-103 Gakuenhigashi-machi,
Nishi-ku
Kobe-shi, Hyogo (JP)
Inventor : **Fukumoto, Takahiro**
5-14-115-302 Nishiochiai,
Suma-ku
Kobe-shi, Hyogo (JP)
Inventor : **Muraoka, Kiyoshige**
1-6-28-404 Shioya-cho,
Tarumi-ku
Kobe-shi, Hyogo (JP)

㉕ Representative : **Stewart, Charles Geoffrey**
SP TYRES UK LIMITED
Technical Division
Fort Dunlop, Erdington, Birmingham B24 9QT
(GB)

⑤④ Rubber composition for a steel belt of a tyre.

⑤⑦ A rubber composition for a steel belt of a tyre particularly for improved steering stability and reduced rolling resistance comprising: 100 parts by weight of a diene rubber containing at least either one of natural rubber and polyisoprene as a main component thereof; 60 to 90 parts by weight of a carbon black having an iodine adsorption of 50 to 100 mg/g and a dibutylphthalate absorption of 100 to 160 ml/100g; 5 to 6 parts by weight of sulfur; 1.5 to 3 parts by weight of a sulfenamide-based vulcanisation accelerator; 2 to 5 parts by weight of a modified methylolmelamine resin; and 2 to 5 parts by weight of a modified resorcinolformaldehyde.

FIG. 1



EP 0 675 161 A1

The present invention relates to rubber compositions for a steel belt of a tyre for a vehicle and, more particularly, to rubber compositions for steel belts which satisfy requirements for improved steering stability and reduced rolling resistance.

With the recent performance improvement of vehicles, one performance requirement of tyres is to provide improved steering stability. One method that meets such requirement is to increase the hysteresis loss of the tread rubber to improve the gripping force against the road surface. However, tread rubber compositions having a greater hysteresis loss tend to deteriorate the rolling resistance of a tyre.

A tyre includes a belt 3 (or breaker) having a width nearly equal to a tread width and interposed between a carcass portion 2 and a tread portion 1. The belt 3 serves to radially compress the entire tyre as well as to maintain the circumferential rigidity of the tyre. Therefore, the steering stability can be ensured by employing less stretchable and highly rigid belt 3.

It is, therefore, an object of the present invention to provide a rubber composition for a steel belt which can provide improved steering stability and rolling resistance.

The inventors of the present invention have found that requirements for improved steering stability and for reduced rolling resistance can both be satisfied by improving the rubber composition which is to be disposed around a belt made of steel (hereinafter referred to as "rubber for steel belt"), and hence attained the present invention.

According to the present invention a rubber composition for a steel belt comprises: 100 parts by weight of a diene rubber containing at least either one of natural rubber and polyisoprene as a main component thereof; 60 to 90 parts by weight of a carbon black having an iodine adsorption of 50 to 100 mg/g and a dibutylphthalate absorption of 100 to 160 ml/100g; 5 to 6 parts by weight of sulfur; 1.5 to 3 parts by weight of a sulfenamide-based vulcanisation accelerator; 2 to 5 parts by weight of a modified methylolmelamine resin; and 2 to 5 parts by weight of a modified resorcinolformaldehyde.

Various other objects, features and attendant advantages of the present invention will be more fully appreciated as the same becomes better understood from the following detailed description in conjunction with the attached drawing in which:

Figure 1 is a sectional view of a tyre.

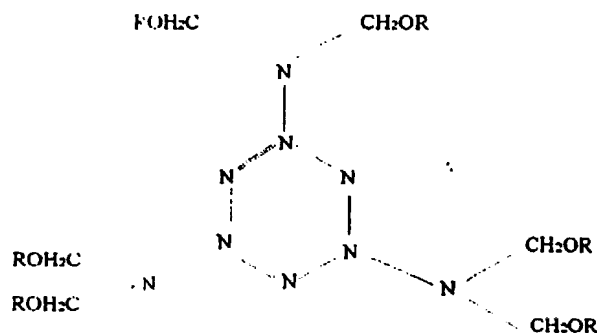
A carbon black to be blended in the rubber composition of the present invention has an iodine adsorption of 50 to 100 mg/g and a dibutylphthalate absorption (hereinafter referred to as "DBP absorption") of 100 to 160 ml/100g. A carbon black having an iodine adsorption of less than 50 mg/g is not used, because such carbon black reduces the elasticity modulus of the rubber composition and hence deteriorates steering stability of the tyre. A carbon black having an iodine adsorption of greater than 100 mg/g is also not used, because such carbon black deteriorates the workability and dispersibility on kneading or mixing the rubber composition, and results in a loss tangent of the rubber composition so high that the rolling resistance of the tyre is poor. A DBP absorption of less than 100 ml/100g results in a rubber composition having a low elasticity modulus so that the steering stability cannot be sufficiently improved. On the other hand, a DBP absorption of greater than 160 ml/100g results in a rubber composition having an excessively high elasticity so that the durability of the tyre is deteriorated. In addition, the loss tangent of such rubber composition is so high that the rolling resistance of the tyre is degraded. Therefore a DBP absorption of less than 100 ml/100g or greater than 160 ml/100g is not used.

The blending ratio of the carbon black having the aforesaid properties is 60 to 90 parts by weight relative to 100 parts by weight of the rubber component. If the blending ratio is less than 60 phr, the elasticity modulus of the rubber composition is too low to sufficiently improve the steering stability. On the other hand, if the blending ratio is greater than 90 phr, the elasticity modulus of the rubber composition is so high that the steering stability is deteriorated. In addition, the loss tangent of the rubber composition is increased, thereby degrading the rolling resistance of the tyre. Therefore, a blending ratio of less than 60 phr or greater than 90 phr is not preferable.

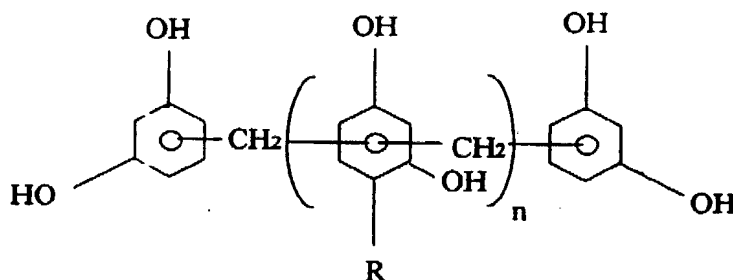
The blending ratio of sulfur is 5 to 6 parts by weight relative to 100 parts by weight of the rubber component. If the blending ratio is less than 5 phr, the adhesion of the rubber composition to steel cord is insufficient, thereby deteriorating the durability of tyres. Furthermore, the loss tangent of the rubber composition is increased, thereby degrading the rolling resistance of the tyre. On the other hand, if the blending ratio is greater than 6 phr, blooming of excessive sulfur occurs, so that the workability of the rubber composition is deteriorated. Therefore, a blending ratio of less than 5 phr or greater than 6 phr is not used.

The blending ratio of the sulfenamide-based vulcanisation accelerator is 1.5 to 3 parts relative to 100 parts of the rubber component. If the blending ratio is less than 1.5 phr, the adhesion of the rubber composition to steel cord is not enough because of insufficient vulcanisation. -If the blending ratio is greater than 3 phr, the elasticity modulus of the rubber composition is so high that the durability of the tyre is deteriorated. Therefore, a blending ratio of less than 1.5 phr or greater than 3 phr is not used.

A modified methylolmelamine resin and a modified resorcinolformaldehyde are added to improve the adhesion of the rubber composition to the steel cord. The modified methylolmelamine resin herein is obtained by way of etherification of a methylolmelamine resin. The monomer unit of the modified methylolmelamine resin is represented by the following formula (1)



The modified resorcinolformaldehyde is obtained by way of alkylation of a resorcinolformaldehyde, and is represented by the following formula (2):



A curing reaction between a methylene group (methylene donor) of the modified methylolmelamine resin and a hydroxyl group (methylene acceptor) of the modified resorcinolformaldehyde contributes to the adhesion of the rubber composition to the steel cord. This adhesive effect increases the complex elasticity modulus of the rubber composition co-operatively with the vulcanisation of the rubber itself, thereby reducing the loss tangent. The ratio of the modified methylolmelamine resin to the modified resorcinolformaldehyde is preferably from 1:1 to 2:1. The blending ratio of each of the resins in the rubber composition is preferably 2 to 5 parts by weight relative to 100 parts of the rubber component. If the blending ratio of each of the resins is greater than 5 phr, the curing rate becomes higher (or scorching time becomes shorter), thereby deteriorating the workability of the rubber composition.

In addition to the aforesaid compounds, additives generally used in the rubber industry may, as required, be added to the rubber composition of the present invention. For example, 0.5 to 5 parts of an organic cobalt salt is preferably blended in the rubber composition. The organic cobalt salt serves to crosslink the rubber component and steel cord increasing the adhesive force between the rubber component and steel cord, thereby contributing to an improvement of the durability of tyres. However, if the amount of organic cobalt salt is excessive, more specifically, the blending ratio thereof is greater than 5 phr, deterioration of the rubber composition due to oxidation occurs. As well as the organic cobalt salt, there may, as required, be added antioxidant, softening agent, zinc white, stearic acid or a like additive.

The foregoing rubber composition, especially, obtained after the vulcanisation preferably has such rubber properties that the complex elasticity modulus is 18.0 to 28.0 MPa and the loss tangent is 0.07 to 0.12. In general, a complex elasticity modulus of less than 18.0 MPa does not ensure sufficient steering stability, and a complex elasticity modulus of greater than 28.0 -MPa is liable to deteriorate the vehicle-riding comfort and to

reduce the durability of the tyre. Therefore, a complex elasticity modulus of less than 18.0 MPa or greater than 28.0 MPa is not preferable. On the other hand, a loss tangent of less than 0.07 results in unstable steering performance, while a loss tangent of greater than 0.12 degrades the rolling resistance. Therefore, a loss tangent of less than 0.07 or greater than 0.12 is not preferable.

The rubber composition for steel belt of the aforesaid composition thus described allows the steering stability of a vehicle to be improved without increasing the rolling resistance of a tyre. Therefore, the use of rubber composition for steel belt in accordance with the present invention makes it possible to build tyres that satisfy requirements for the rolling resistance, steering stability and riding comfort.

The rubber composition of the present invention will hereinafter be more specifically described by way of the following specific examples. It should be noted that these examples are not limiting of the present invention.

Rubber compositions in accordance with Example 1 to 4 and Reference Example 1 to 8 were each prepared by blending substances as shown in Table 1 in a blending ratio as shown also in Table 1. Among these rubber compositions, Reference Example 1 is a rubber composition which is now typically used for steel belt.

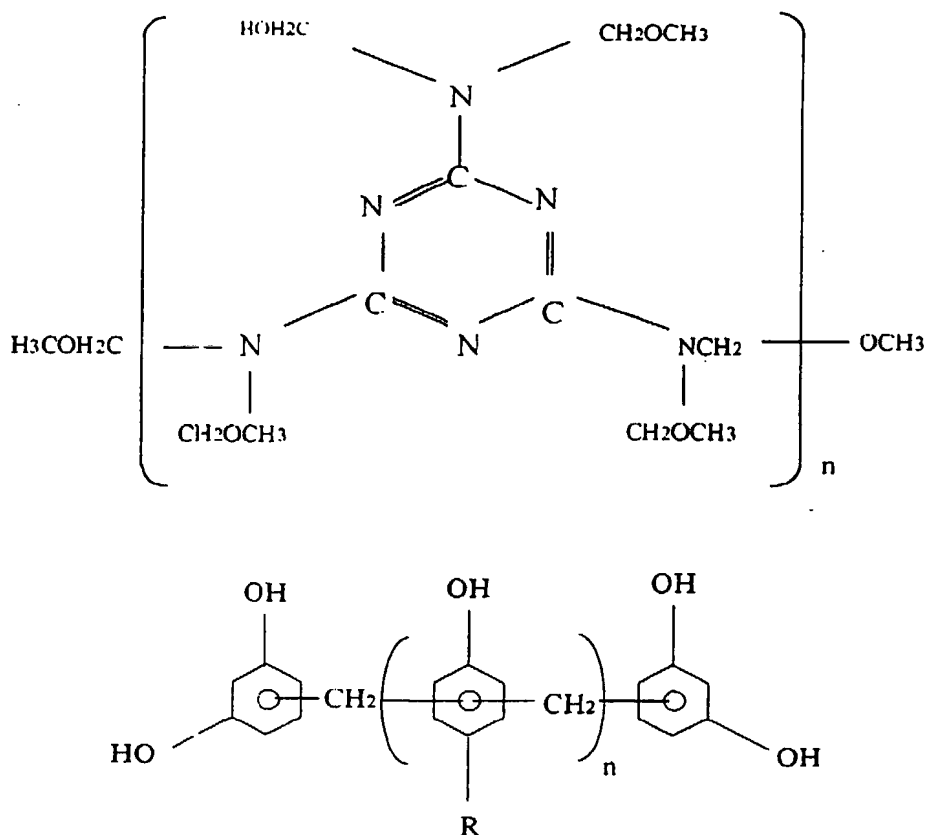
Table 1

Rubber compositions	Examples				Reference Examples							
	1	2	3	4	1	2	3	4	5	6	7	8
Natural rubber	100	100	100	80	100	100	100	100	100	100	100	100
Isoprene rubber	-	-	-	20	-	-	-	-	-	-	-	-
Carbon black A	-	-	-	-	-	-	80	-	-	-	-	-
Carbon black B	60	60	80	60	60	60	-	-	80	80	95	50
Carbon black C	-	-	-	-	-	-	-	80	-	-	-	-
Insoluble sulfur	6	6	6	6	4	6	6	6	4	7	6	6
Vulcanisation accelerator	2.5	2.5	2.5	2.5	1	2.5	2.5	2.5	1	4	2.5	2.5
Modified methylolmelamine resin	3	5	5	5	-	-	5	5	5	5	3	3
Modified resorcinolformaldehyde resin	3	3	3	3	-	-	3	3	3	3	3	3
Cobalt naphthenate	2	2	2	2	2	2	2	2	2	2	2	2
Antioxidant	1	1	1	1	1	1	1	1	1	1	1	1

Table 2

Carbon black	Iodine adsorption	DBP absorption
(name)	(mg/g)	(ml/100g)
A (N219)	118	78
B (N351)	68	120
C (N550)	43	121

The properties of the carbon blacks A, B and C shown in Table 1 are shown in Table 2. As can be understood therefrom, the carbon Black B satisfies the requirement of the present invention. Poly-(2,2,4-trimethyl-1,2-dihydroquinoline) and N,N-dicyclohexyl-2-benzothiazolylsulfenamide were used as the antioxidant and vulcanising agent, respectively. SUMIKANOL 507 (represented by the formula (3)) and SUMIKANOL 620 (represented by the formula (4)) both available from Sumitomo Chemical Co Limited were used as the modified methylolmelamine resin and modified resorcinolformaldehyde resin, respectively.



SUMIKANOL 507 is a mixture of a partial condensate of hexamethylolmelamine pentamethyl ether and silica, and the content of silica is 50% by weight.

These rubber compositions were vulcanised under the same conditions to prepare vulcanised rubber test strips. Then, the complex elasticity moduli (E^*) and loss tangents ($\tan\delta$) of the respective vulcanised rubber test strips were measured by means of a viscoelasticity spectrometer (Iwamoto Selsakusho Co) with a frequency of 10 Hz and a dynamic strain of 2% at a temperature of 70°C.

In turn, tyres (185/65R14) were built using the aforesaid respective rubber compositions as the topping or coating rubber for the steel belt. Each set of tyres were fitted in turn to a vehicle (FR car made in Japan), and then the ride comfort, steering stability during lane changing of the vehicle and rolling resistance were measured. The measured results are shown in Table 3. The ride comfort and steering stability were determined by sensory evaluation using a ten-level rating (1 to 10), and ratings of not lower than 6 were regarded as passing the test. The rolling resistance was represented by an index calculated with the rolling resistance of Reference Example 1 being 100. A smaller index means a smaller rolling resistance, and is considered to be more preferable.

Table 3

Rubber compositions	Examples			
	1	2	3	4
Viscoelasticity				
E*	22.5	24.5	27.0	24.0
tan δ	0.08	0.08	0.11	0.08
Tyre performance				
Rolling resistance	100	100	101	100
Steering stability	6	6	7	6
Riding comfort	6	6	6	6

Rubber compositions	Reference examples							
	1	2	3	4	5	6	7	8
Viscoelasticity								
E*	7.8	12.4	30.7	16.5	24.5	30.0	25.4	16.0
tan δ	0.13	0.07	0.16	0.09	0.20	0.09	0.20	0.06
Tyre performance								
Rolling resistance	100	98	105	100	105	102	106	98
Steering stability	5	5	7	5	7	6	7	5
Riding comfort	7	7	5	6	6	5	4	6

As can be understood from Table 3, where the complex elasticity modulus is 18.0 or less or where the loss tangent is 0.7 or less, the steering stability is insufficient. On the other hand, where the complex elasticity modulus is 28.0 or greater or where the loss tangent is 0.12 or greater, the rolling resistance is undesirably high and the riding comfort is degraded.

As can be understood from the comparison between Examples 2 and 4 and Reference Examples 3 and 4 shown in Table 3, the complex elasticity modulus E* and loss tangent tan δ can be maintained in a desired range by blending the carbon black B having an iodine adsorption of 40 to 100 mg/g in the rubber composition, and thus the requirements for steering stability, rolling resistance and riding comfort can be satisfied. An excessively high blending ratio of the carbon black B results in a high loss tangent tan δ and a high rolling resistance, thereby deteriorating the riding comfort (see examples 1 to 4 and reference example 7). An excessively low blending ratio of the carbon black B results in a low complex elasticity modulus E* and an excessively low rolling resistance, thereby deteriorating the steering stability (see examples 1 to 4 and reference example 8).

As can be understood from the comparison between Example 3 and Reference Example 5, where the contents of both sulfur and sulfenamide-based vulcanisation accelerator are small, the vulcanisation of the rubber composition is insufficient, and results in the likelihood of increased loss tangent tan δ and rolling resistance.

Further, as can be appreciated from the comparison between Examples 1, 2 and 4 and Reference Example 2, the complex elasticity modulus E* and loss tangent tan δ can be improved by blending the modified methylolmelamine resin and modified resorcinolformaldehyde in respective predetermined amounts in the rubber composition.

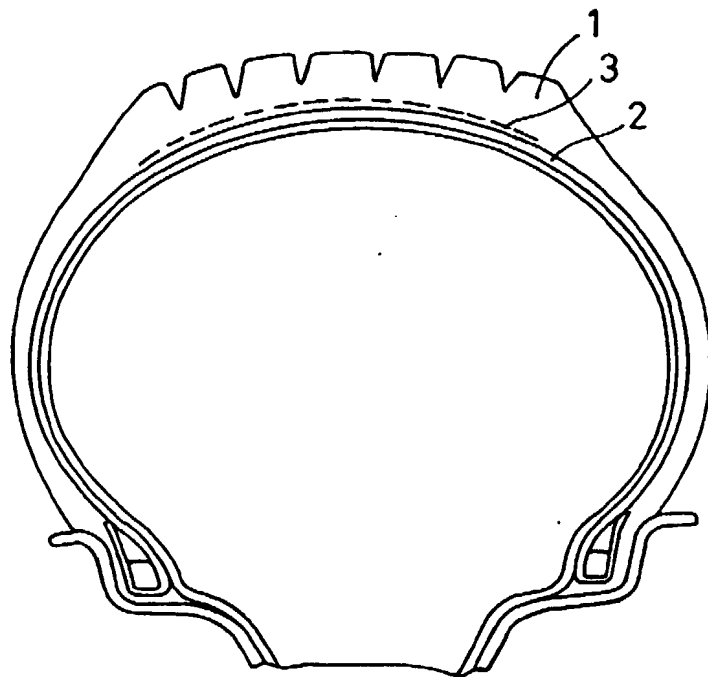
Claims

1. A rubber composition for a steel belt for a tyre, comprising 100 parts by weight of a diene rubber containing at least either one of natural rubber and polyisoprene as a main component thereof; 60 to 90 parts by weight of a carbon black having an iodine adsorption of 50 to 100 mg/g and a dibutylphthalate absorption of 100 to 160 ml/100g; 5 to 6 parts by weight of sulfur; 1.5 to 3 parts by weight of a sulfenamide-based vulcanisation accelerator; 2 to 5 parts by weight of a modified methylolmelamine resin; and 2 to 5 parts

by weight of a modified resorcinolformaldehyde.

2. A rubber composition for a steel belt as set forth in claim 1, characterised in that the blending ratio of said modified methylolmelamine resin to said modified resorcinolformaldehyde resin is 1:1 to 2:1.
3. A rubber composition for a steel belt- as set forth in claim 1 or 2, characterised by 0.5 to 5 parts by weight of an organic cobalt salt.
4. A rubber composition for a steel belt as set forth in any claims 1 to 3, characterised in that a complex elasticity modulus of 18.0 to 28.0 MPa and a loss tangent of 0.07 to 0.12.
5. A rubber composition for a steel belt as set forth in any of claims 1 to 4, characterised in that the blending ratio of said modified methylolmelamine resin to said modified resorcinolformaldehyde resin is 1:1 to 2:1.
6. A rubber composition for a steel belt as set forth in any of claims 1 to 5, characterised by 0.5 to 5 parts by weight of an organic cobalt salt.
7. A tyre comprising a rubber composition as recited in claims 1 to 6, which is disposed around a steel belt and vulcanised.

FIG. 1





European Patent
Office

EUROPEAN SEARCH REPORT

Application Number
EP 95 30 2025

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int.Cl.6)
X	DE-A-41 18 180 (THE YOKOHAMA RUBBER CO) * page 2, line 37 - line 42; claims; tables * -----	1,3,6,7	C08L7/00 C08L9/00 B60C9/20
			TECHNICAL FIELDS SEARCHED (Int.Cl.6)
			C08L B60C
The present search report has been drawn up for all claims			
Place of search THE HAGUE		Date of completion of the search 5 July 1995	Examiner Van Humbeeck, F
<p>CATEGORY OF CITED DOCUMENTS</p> <p>X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document</p> <p>T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons & : member of the same patent family, corresponding document</p>			

EPO FORM 1503 01.82 (P04C01)